

PCT

WORLD INTELLECTUAL PROPERTY ORGANIZATION  
International Bureau



INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

<p>(51) International Patent Classification <sup>7</sup> : B05D 7/02, 7/04, B32B 7/10, 31/12, C08J 5/12, 7/04, B32B 31/00</p>	<p>A1</p>	<p>(11) International Publication Number: WO 00/48749 (43) International Publication Date: 24 August 2000 (24.08.00)</p>
<p>(21) International Application Number: PCT/US00/03362 (22) International Filing Date: 8 February 2000 (08.02.00) (30) Priority Data: 09/252,904 18 February 1999 (18.02.99) US (71) Applicant: BATTELLE MEMORIAL INSTITUTE [US/US]; Pacific Northwest Division, Intellectual Property Services, P.O. Box 999, Richland, WA 99352 (US). (72) Inventors: EUFINGER, Stephan; TC BAM/CVO, NV Bekaert, Bekaertstraat 2/6030, B-8550 Zwevegem (BE). AFFINITO, John, D.; 2718 Kyle Road, Kennewick, WA 99338 (US). GROSS, Mark, E.; 50 Deseret Drive, Pasco, WA 99301 (US). (74) Agent: MAY, Stephen, R.; Battelle Memorial Institute, Pacific Northwest Division, Intellectual Property Services, P.O. Box 999, MSIN: K1-53, Richland, WA 99352 (US).</p>		<p>(81) Designated States: JP, KR, European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).  Published With international search report.</p>
<p>(54) Title: METHOD FOR ADHERING LAMINATE STRUCTURES</p>		
<p>(57) Abstract</p> <p>It has been discovered that a combination of a reactive compound in the monomer in combination with a contact surface activating plasma achieves maximum lamination strength for a polymer/second layer laminate for vacuum lamination. This is true whether the second layer is placed upon the polymer layer or whether the monomer is placed upon the second layer then polymerized as the polymer in a vacuum.</p> <div data-bbox="560 1155 1331 1554"> </div>		

*FOR THE PURPOSES OF INFORMATION ONLY*

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AL	Albania	ES	Spain	LS	Lesotho	SI	Slovenia
AM	Armenia	FI	Finland	LT	Lithuania	SK	Slovakia
AT	Austria	FR	France	LU	Luxembourg	SN	Senegal
AU	Australia	GA	Gabon	LV	Latvia	SZ	Swaziland
AZ	Azerbaijan	GB	United Kingdom	MC	Monaco	TD	Chad
BA	Bosnia and Herzegovina	GE	Georgia	MD	Republic of Moldova	TG	Togo
BB	Barbados	GH	Ghana	MG	Madagascar	TJ	Tajikistan
BE	Belgium	GN	Guinea	MK	The former Yugoslav Republic of Macedonia	TM	Turkmenistan
BF	Burkina Faso	GR	Greece			TR	Turkey
BG	Bulgaria	HU	Hungary	ML	Mali	TT	Trinidad and Tobago
BJ	Benin	IE	Ireland	MN	Mongolia	UA	Ukraine
BR	Brazil	IL	Israel	MR	Mauritania	UG	Uganda
BY	Belarus	IS	Iceland	MW	Malawi	US	United States of America
CA	Canada	IT	Italy	MX	Mexico	UZ	Uzbekistan
CF	Central African Republic	JP	Japan	NE	Niger	VN	Viet Nam
CG	Congo	KE	Kenya	NL	Netherlands	YU	Yugoslavia
CH	Switzerland	KG	Kyrgyzstan	NO	Norway	ZW	Zimbabwe
CI	Côte d'Ivoire	KP	Democratic People's Republic of Korea	NZ	New Zealand		
CM	Cameroon			PL	Poland		
CN	China	KR	Republic of Korea	PT	Portugal		
CU	Cuba	KZ	Kazakstan	RO	Romania		
CZ	Czech Republic	LC	Saint Lucia	RU	Russian Federation		
DE	Germany	LI	Liechtenstein	SD	Sudan		
DK	Denmark	LK	Sri Lanka	SE	Sweden		
EE	Estonia	LR	Liberia	SG	Singapore		

## METHOD FOR ADHERING LAMINATE STRUCTURES

5

### FIELD OF THE INVENTION

The present invention relates to a method and apparatus for adhering laminate structures. More specifically, the invention relates to a combination of a reactive compound within a monomer and a surface activating plasma to provide an activated surface for adhering a second laminate layer via vacuum deposition to the polymer layer.

### BACKGROUND OF THE INVENTION

15

In many industrial processes non-polymer thin films including but not limited to metals, metal-oxides, semiconductors and combinations thereof are placed on polymer thin films in the form of substrates and/or layers. These thin film combinations are prepared *in-situ* by a number of methods including but not limited to extrusion, flash-evaporation, spraying, blading, plasma enhanced chemical vapor deposition (PECVD), sputtering, evaporation and combinations thereof. The adhesion of these thin film combinations is commonly variable depending upon substrate, deposition method and materials deposited. Therefore treatments such as plasma discharges and/or irradiation with electrons, ultraviolet or laser are routinely employed to activate either the thin film or the polymeric surface or both to promote improved adhesion. However, these methods provide variable levels of strength adhesion and for some material combinations, very low or no strength adhesion based upon a tape pull test.

25  
30

Accordingly there is a need for a method and apparatus to provide greater lamination strength for laminate structures as well as less variability between alternative laminations.

## SUMMARY OF THE INVENTION

It has been discovered that a combination of a reactive compound in the monomer in combination with a contact surface activating plasma achieves  
5 maximum lamination strength for a laminate. This is true whether the second layer is placed upon the polymer layer or whether the monomer is placed upon the second layer then polymerized as the polymer when the contact is made with vacuum deposition.

It is an object of the present invention to achieve superior adhesion  
10 between a polymer and a second layer by adding a reactive compound to the polymer and by activating a contact surface with a plasma in a vacuum.

The subject matter of the present invention is particularly pointed out and distinctly claimed in the concluding portion of this specification. However, both the organization and method of operation, together with further advantages and  
15 objects thereof, may best be understood by reference to the following description taken in connection with accompanying drawings wherein like reference characters refer to like elements.

## BRIEF DESCRIPTION OF THE DRAWINGS

20

FIGURE is a cross section of a reflector made and tested as Example 1.

## DESCRIPTION OF THE PREFERRED EMBODIMENT(S)

25 The present invention is a method and apparatus for of adhering a polymer layer to a second layer which rely upon a combination of

- (a) a reactive compound in the polymer layer;
- (b) a contact surface selected from the group consisting of a polymer contact surface, a second layer contact surface and combinations  
30 thereof exposed to a surface activating plasma and providing an activated contact surface; and

(c) contacting the second layer contact surface to the polymer contact surface in a vacuum, one or the other or both of which is the activated contact surface, thereby adhering the second layer with the polymer layer.

5 The polymer contains an additive that provides one side of a chemical hook that connects with the species provided from the plasma on the second layer contact surface as the other side of the chemical hook. Thus, the adhesion is achieved by selection of additive/plasma species combinations. More specifically, the connection is achieved with a donor acceptor reaction, preferably a base-acid  
10 reaction. For example silicone with a plasma containing oxygen and hydrogen provides OH groups that bind to the silicone. Amine functionalities may be useful for other applications. It is preferred that the acid and base be organic. Preferred organic acids contain a CO= structure, for example carboxylic acids including formic acid, acetic acid, oxalic acid butyric acid; ketones; esters; amino  
15 acids; aldehydes; and combinations thereof. Preferred base has OH, but may have NH or SH groups, for example amines, mercaptans and combinations thereof.

Several combinations are possible. One combination is by adding the reactive compound to a monomer as a monomer mixture. The monomer mixture  
20 may be placed on a substrate via any method including but not limited to extrusion, flash-evaporation, spraying, blading and combinations thereof then polymerized to provide a polymer surface for receiving the non-polymer. Alternatively, the monomer mixture may be placed upon the second layer then polymerized in-situ on the second layer. In either case, the solid surface is  
25 plasma treated prior to contact with the other material.

A vacuum is defined herein as having a pressure less than atmospheric pressure wherein processes including but not limited to sputtering, flash evaporation, plasma enhanced chemical vapor deposition, evaporation and combinations thereof may be conducted.

30 In a preferred embodiment, the monomer is acrylate or methacrylate. Other monomers are possible including but not limited to allyls (double bond), alkynes (triple bond) for example phenyl acetylene. For acrylate or methacrylate

monomer/polymer, the reactive compound may be acrylated silicone. The amount of reactive compound must be sufficient to provide enough reactive material at a surface to provide a strong bond. It has been found that an effective amount of reactive compound is less than about 10 wt%.

5       The second layer may be another layer of the same polymer composition as the polymer layer. Alternatively, the second layer may be a metal, ceramic or combination thereof. Metal includes but is not limited to silver, copper, nickel, aluminum, iron, and combinations thereof. Ceramic includes metal oxides, metal nitrides, silicon oxides, metal carbides and combinations  
10   thereof.

When the additive contains silicone and the plasma contains hydrogen and oxygen, OH groups are formed. The surface activating plasma may be a single compound plasma for example water. However, in some cases water is difficult to maintain as a plasma so a ballast gas may be desired, for example  
15   argon. Because it has been found that a combination of hydrogen and oxygen provides good surface activation, a two-compound plasma of hydrogen and oxygen may also be used for forming the OH groups. The particular combination of plasma gases is specific to the additive and to the second contact surface. For a polymer surface, an argon/water plasma is effective to activate the polymer  
20   surface when silicone is the additive. For a metallic non-polymer surface, an oxygen/hydrogen plasma has the advantage of avoiding water condensation in the delivery system.

The stoichiometric ratio of oxygen to hydrogen is 1:1. Because it is desired to minimize the amount of gas in the system, it is preferred to operate at  
25   or near the stoichiometric amount.

When using a substrate containing oxygen atoms, for example PET, to receive a monomer mixture having silicone therein, it is sufficient that the substrate be plasma treated with a low-intensity argon plasma because the argon in the plasma activate the oxygen in the substrate.

30

### EXAMPLE 1

An experiment was conducted to demonstrate adhesion of silver with polymer with and without the elements of the present invention.

Silver reflectors having a laminate composition of PET substrate, flash evaporated acrylate layer 1, silver layer, and flash evaporated acrylate layer 2 were made.

A silver reflector made with no reactive compound and no plasma surface treatment had such poor adhesion that tape pull tests resulted in complete delamination or removal of the top polymer layer from the silver layer. In a subsequent pull test, the silver came off of the bottom polymer layer.

A silver reflector made with plasma treated surfaces gave the same delamination/removal results with the pull test as the untreated surfaces.

A silver reflector made with reactive compound added to the monomer/polymer gave the same delamination/removal results as the untreated surfaces.

A silver reflector **100** was made according to the present invention (**FIGURE**) with 5 wt% acrylated silicone (Ebecryl 350) as the reactive compound in an acrylate polymer **102**. In addition, a low intensity argon plasma was used to treat the surface **103** of a PET substrate **104** upon which the first monomer layer was flash evaporated and condensed and subsequently polymerized **102**. The polymerized surface **106** was exposed to an argon/water plasma for surface activation prior to putting down the silver layer **108** by sputtering. The top silver surface **110** was further activated with a oxygen/hydrogen plasma with a ratio of oxygen to hydrogen of 1:1. A second monomer mixture layer **112** was flash evaporated and condensed onto the activated silver layer **110**. Tape pull tests, with or without razor cross hatching, resulted in no delamination or removal of any layer.

### CLOSURE

While a preferred embodiment of the present invention has been shown and described, it will be apparent to those skilled in the art that many changes

and modifications may be made without departing from the invention in its broader aspects. The appended claims are therefore intended to cover all such changes and modifications as fall within the true spirit and scope of the invention.



## CLAIMS

We claim:

- 5           1.     A method of adhering a polymer layer to a second layer,  
comprising the steps of:
- (a)     providing a reactive compound in said polymer layer;
  - (b)     exposing a contact surface selected from the group  
10       consisting of a polymer contact surface, a second layer contact surface  
and combinations thereof to a surface activating plasma and providing an  
activated contact surface; and
  - (c)     contacting said second layer contact surface to said polymer  
15       contact surface in a vacuum, one or the other or both of which is said  
activated contact surface, thereby adhering the second layer with the  
polymer layer.
2.     The method as recited in claim 1, wherein said providing is by  
adding said reactive compound to a monomer as a monomer mixture.
- 20          3.     The method as recited in claim 2, wherein said polymer surface is  
formed by polymerizing said monomer mixture.
4.     The method as recited in claim 2, wherein said contacting is by  
placing said monomer mixture onto said non-polymer followed by polymerization  
25       of said monomer mixture, and wherein said activated surface is said second  
layer contact surface.
5.     The method as recited in claim 1, wherein said reactive  
30       compound is acrylated silicone.
6.     The method as recited in claim 5, wherein said polymer contact  
surface is activated with an argon/water plasma.

7. The method as recited in claim 5, wherein said second layer contact surface is silver.

5 8. The method as recited in claim 7 wherein said surface activating plasma is selected from the group consisting of oxygen/hydrogen, water, and combinations thereof.

9. The method as recited in claim 8 wherein said surface activating  
10 plasma includes a noble gas.

10. The method as recited in claim 9, wherein said noble gas is argon.

15 11. The method as recited in claim 1, wherein said contacting is selected from the group consisting of sputtering, flash evaporation, plasma enhanced chemical vapor deposition, evaporation and combinations thereof.

12. A method of adhering a polymer to a second layer, comprising the  
20 steps of:

(a) adding a reactive compound to a monomer as a monomer mixture and polymerizing the monomer mixture to said polymer layer;

(b) activating said reactive compound at a surface of said polymer by exposing said surface to a polymer surface activating plasma, and  
25 providing an activated polymer surface; and

(c) contacting said activated polymer surface with said second layer whereupon bonding adheres said second layer to said polymer.

13. The method as recited in claim 12, wherein said reactive  
30 compound is acrylated silicone.

14. The method as recited in claim 12, wherein said polymer surface activating plasma is an argon/water plasma.

15. A method of adhering a second layer to a polymer, comprising the  
5 steps of:

(a) activating a surface of said second layer by exposing said surface to a second layer surface activating plasma, and providing an activated surface;

(b) adding a reactive compound to a monomer as a monomer  
10 mixture and contacting said monomer mixture with said activated surface; and

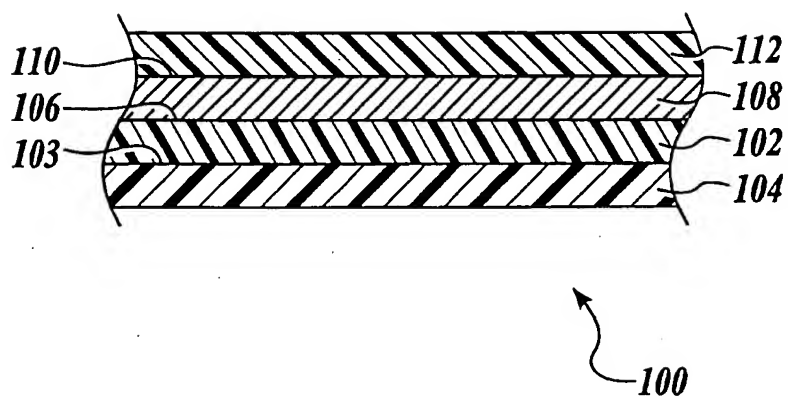
(c) polymerizing said monomer mixture

16. The method as recited in claim 15, wherein said reactive compound is acrylated silicone.

15

17. The method as recited in claim 15, wherein said second layer surface activating plasma is an oxygen/hydrogen plasma.

18. The method as recited in claim 15, wherein said contacting is  
20 selected from the group consisting of sputtering, flash evaporation, plasma enhanced chemical vapor deposition, evaporation and combinations thereof.



## INTERNATIONAL SEARCH REPORT

Internal Application No

PCT/US 00/03362

## A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 B05D7/02 B05D7/04 B32B7/10 B32B31/12 C08J5/12  
C08J7/04 B32B31/00

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 B05D B32B C08J

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0 547 550 A (MATSUSHITA ELECTRIC IND CO LTD) 23 June 1993 (1993-06-23) claims 2,8	1-18
X	WO 95 10117 A (CATALINA COATINGS INC ; SHAW DAVID G (US); DAWSON ERIC (US); CLINE) 13 April 1995 (1995-04-13) claim 8	1-18
X	WO 98 18852 A (CATALINA COATINGS INC ; DAWSON ERIC P (US); LANGLOIS MARC (US); CLI) 7 May 1998 (1998-05-07) claims 1,8	1-18
-/--		



Further documents are listed in the continuation of box C.



Patent family members are listed in annex.

## \* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&amp;" document member of the same patent family

Date of the actual completion of the international search

5 May 2000

Date of mailing of the international search report

16/05/2000

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2  
NL - 2280 HV Rijswijk  
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,  
Fax: (+31-70) 340-3016

Authorized officer

Natus, G

## INTERNATIONAL SEARCH REPORT

International Application No.

PCT/US 00/03362

## C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0 722 787 A (CATALINA COATINGS INC) 24 July 1996 (1996-07-24) column 6, line 23-26 column 7, line 22-24 column 9, line 37-50	1-18
X	EP 0 787 826 A (BECTON DICKINSON CO) 6 August 1997 (1997-08-06) claim 15	1-18
P,X	EP 0 931 850 A (LEYBOLD SYSTEMS GMBH) 28 July 1999 (1999-07-28) column 3, line 50-57 column 5, line 10-26	1-18
X	EP 0 590 467 A (ROEHM GMBH ;FRAUNHOFER GES FORSCHUNG (DE)) 6 April 1994 (1994-04-06) claim 1; examples 1-5	1-18
X	PATENT ABSTRACTS OF JAPAN vol. 1997, no. 04, 30 April 1997 (1997-04-30) & JP 08 325713 A (MATSUSHITA ELECTRIC WORKS LTD), 10 December 1996 (1996-12-10) abstract	1-18
X	PATENT ABSTRACTS OF JAPAN vol. 1997, no. 07, 31 July 1997 (1997-07-31) & JP 09 059763 A (MATSUSHITA ELECTRIC WORKS LTD), 4 March 1997 (1997-03-04) abstract	1-18
X	WO 97 22631 A (TALISON RESEARCH) 26 June 1997 (1997-06-26) claims 1,3	1-18
X	PATENT ABSTRACTS OF JAPAN vol. 012, no. 396 (P-774), 21 October 1988 (1988-10-21) & JP 63 136316 A (HITACHI LTD), 8 June 1988 (1988-06-08) abstract	12-18
X	US 5 576 101 A (SAITOH SHINJI ET AL) 19 November 1996 (1996-11-19) Abstract	12-18

# INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No.

PCT/US 00/03362

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
EP 0547550	A	23-06-1993	JP 2603017 B	23-04-1997
			JP 5161844 A	29-06-1993
			JP 5168913 A	02-07-1993
			DE 69224888 D	30-04-1998
			DE 69224888 T	23-07-1998
			KR 9701519 B	11-02-1997
			US 5372851 A	13-12-1994
WO 9510117	A	13-04-1995	US 5440446 A	08-08-1995
			AU 694143 B	16-07-1998
			AU 7965594 A	01-05-1995
			BR 9407741 A	12-02-1997
			EP 0758482 A	19-02-1997
			EP 0722787 A	24-07-1996
			FI 961478 A	02-04-1996
			JP 8512256 T	24-12-1996
			US 5725909 A	10-03-1998
WO 9818852	A	07-05-1998	AU 5100298 A	22-05-1998
			CN 1238792 A	15-12-1999
			EP 0935633 A	18-08-1999
EP 0722787	A	24-07-1996	US 5440446 A	08-08-1995
			AU 694143 B	16-07-1998
			AU 7965594 A	01-05-1995
			BR 9407741 A	12-02-1997
			EP 0758482 A	19-02-1997
			FI 961478 A	02-04-1996
			JP 8512256 T	24-12-1996
			WO 9510117 A	13-04-1995
			US 5725909 A	10-03-1998
EP 0787826	A	06-08-1997	DE 4430777 A	07-03-1996
			US 5955161 A	21-09-1999
			AU 1232397 A	07-08-1997
			CA 2194636 A	31-07-1997
			JP 9253077 A	30-09-1997
			SG 43456 A	17-10-1997
			US 5775579 A	07-07-1998
			BR 9700742 A	03-11-1998
			KR 188289 B	01-06-1999
EP 0931850	A	28-07-1999	DE 19802740 A	29-07-1999
EP 0590467	A	06-04-1994	DE 4232390 A	31-03-1994
			AT 166901 T	15-06-1998
			DE 59308639 D	09-07-1998
			ES 2118866 T	01-10-1998
JP 08325713	A	10-12-1996	NONE	
JP 09059763	A	04-03-1997	NONE	
WO 9722631	A	26-06-1997	US 5723219 A	03-03-1998
			CA 2213328 A	26-06-1997
			EP 0809659 A	03-12-1997
			US 5962138 A	05-10-1999

# INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US 00/03362

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
JP 63136316 A	08-06-1988	JP 7105034 B	13-11-1995
US 5576101 A	19-11-1996	JP 6182935 A	05-07-1994
		DE 4343027 A	23-06-1994